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Homo-dinuclear σ-alkynyl complexes: past, present and opportunities

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Abstract

Homo-dinuclear alkynyl complexes with a distinct metal–metal bond constitute a rapidly growing field, where the focus is placed on compounds based on ruthenium, molybdenum, tungsten or rhodium. Interesting characteristics of these complexes include paramagnetism, intense charge-transfer absorptions, tunable bridging ligands, which may not be easily accessible in mononuclear acetylide systems. These complexes have significant potential for use in both molecular electronics and supramolecular chemistry. In this short account, previous work in this area is assessed, and each of the major groups of complexes is discussed in terms of both the synthetic strategies and structural motifs.

Keywords: Dinuclear; Metallaynes; Alkynyl; Metal–metal bonding; Molecular wires

1. Introduction

Two decades have passed since the appearance of the first review on metal alkynyl compounds by Nast [1]. In the intervening period, the number of papers published in the area has increased rapidly, and several reviews and monographs focusing on both the synthesis and structural/bonding aspects of metal alkynyl compounds have appeared [2–6]. In addition, metal alkynyl complexes have attracted attention for practical applications such as nonlinear optics [7,8], luminescent materials [9,10], molecular devices [11,12], and polymer chemistry [13]. Organometallic dinuclear complexes containing a metal–metal bond constitute a burgeoning field of chemistry with several reviews published [14–17]. In particular dinuclear systems containing M–C bonds have served as important models for understanding catalytic behavior [18–20]. Although mononuclear alkynyl complexes have attracted greater attention, bimetallic alkynyl complexes have also been the subjects of significant research. Bimetallic complexes may display different architectural motifs, bridging-ligand configurations, paramagnetism, mixed-valence states and fluxional modes which make them interesting and diverse systems to examine. Although a vast number of bimetallic alkynyl complexes have been synthesized, the scope of our discussion will be restricted to those homonuclear complexes containing a distinct metal–metal bond and at least one σ bonded alkynyl ligand. Dinuclear complexes containing a π-bonded η^2,η'^2-bridging alkyne ligand have been reviewed recently [21].

The main objective of this review is to highlight the developments in the synthesis of dinuclear alkynyl complexes in terms of metal centers and overall structural motifs. Trends among metal centers will be examined wherever possible, and exceptions to general classes noted. Dinuclear alkynyl complexes have already begun to show promise as potential molecular wires and supramolecular synthons, and such recent developments will be discussed. With the large number of new dinuclear complexes synthesized [14,22,23], potential targets for alkynylation chemistry are extensive. While

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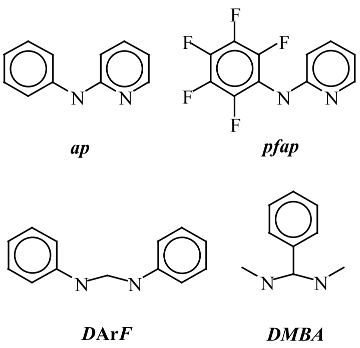
work on diruthenium paddlewheel alkynyl complexes is discussed here, further details can be found in another recent account [24].

2. Diruthenium complexes

A significant number of alkynyl complexes have been synthesized with a diruthenium core supported by several types of bridging ligands, some examples of which are illustrated in Scheme 1. The first synthesis of a diruthenium alkynyl complex was reported by Cotton et al. [25], who isolated $Ru_2(ap)_4(C\equiv CPh)$ (where ap = 2-anilinopyridinate) in ~70% yield from the reaction between $Ru_2(ap)_4Cl$ and five equivalents of lithiated $PhC\equiv CH$. An X-ray crystal structure analysis revealed that the bridging ap ligands adopt a (4,0) arrangement with all four phenyl rings on the opposite side of the bonded phenylacetylide (Fig. 1). The Ru–Ru bond length was 2.319(3) Å, notably longer than that of the parent chloro complex (2.275(3) Å) due to the formation of a strong Ru–C bond at the expense of the Ru–Ru bond. The phenylacetylide complex is paramagnetic with $S = 3/2$. Later work demonstrated an alternative synthetic procedure for $Ru_2(ap)_4(C\equiv CPh)$ via a reaction between $Ru_2(ap)_4Cl$ and $Me_3SnC\equiv CPh$ [26]. The selectivity of this reaction towards the axial halide was also demonstrated through the reactions of $Me_3SnC\equiv CPh$ with $Ru_2(chp)_4Cl$ and $Ru_2(bhp)_4Cl$ (chp = 2-chloro-6-hydroxypyridine and bhp = 2-bromo-6-hydroxypyridine), where axial alkynyl complexes were the only products isolated. The $Ru_2(LL)_4(C\equiv CPh)$ type complexes (LL = chp or bhp) are also of interest in that the bridging ligands contain both nitrogen and oxygen donor centers, while the majority of reported diruthenium acetylide complexes are supported by *N*,*N*′-bidentate bridging ligands. Following Cotton's initial work [25], a series of $Ru_2(ap)_4(C\equiv CY)$ type complexes were synthesized, with Y = $SiMe_3$, H and CH_2COCH_3 [27]. The structural and spectroscopic characterization of these compounds indicated that these new complexes were generally isostructural and isoelectronic with $Ru_2(ap)_4(C\equiv CPh)$. More recently, a new series of mono-substituted $Ru_2(ap)_4$ acetylide complexes were synthesized and included multiple $Ru_2(ap)_4$ units linked through aryl acetylide building blocks [28]. Unexpectedly these complexes did not exhibit any electronic communication between the dimetallic centers.



Scheme 1. Common bridging ligands for paddlewheel diruthenium alkynyl compounds.

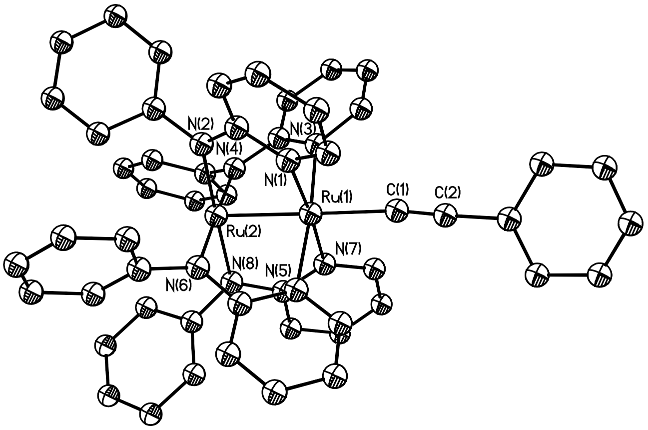
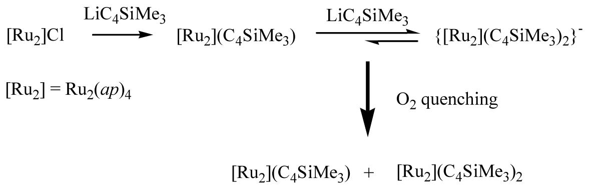


Fig. 1. ORTEP plot of $Ru_2(ap)_4(C_2Ph)$ at 30% probability level generated from the data deposited with CSD [29].

X-ray diffraction studies of $Ru_2(ap)_4(C\equiv CY)$ complexes confirm the (4,0) distribution pattern of the bridging ligands as well as the approximately linear geometry of the alkynyl ligand, a trend which has been consistently observed for this type of complexes [25,27,30]. The electrochemistry of the $Ru_2(ap)_4(C\equiv CY)$ complexes consists of a single reversible oxidation process and one reversible reduction process. Depending on the nature of Y and the solvent, irreversible oxidation couples may also be observed at more positive potentials [27]. The mono-alkynyl $Ru_2(ap)_4$ complexes are brown solids, stable to air and moisture, and can be purified using silica gel chromatography.

Because of the (4,0) arrangement of the ap ligands, the second axial site was initially considered inaccessible due to the steric hindrance of the phenyl rings. Xu et al. reported the first set of mono- and bis-substituted $Ru_2(ap)_4$ butadiynyl complexes, $Ru_2(ap)_4(C\equiv CC\equiv CSiMe_3)_n$ ($n = 1$ and 2) [30]. The work-up conditions are critical to the distribution of products: solvent removal in vacuo resulted in the mono-complex as dominant product, and exposure of reaction solution to air resulted in an enhanced yield of the bis-complex. It

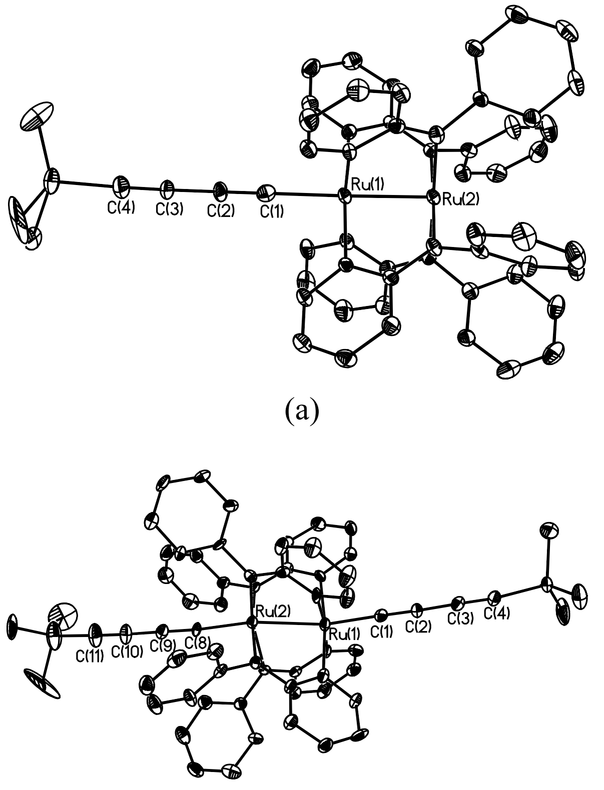


Scheme 2. Reaction equilibrium leading to the formation of mono- and bis-alkynyl $Ru_2(ap)_4$ compounds.

was postulated that a reaction equilibrium described in Scheme 2 was the responsible mechanism [31].

Interestingly, treatment of $Ru_2(ap)_4Cl$ with ten equivalents of $LiC{\equiv}CSiR_3$ ($R = Me$ and ${}^iPr$) led only to the mono-product [32], where the absence of the bis-ethynyl adduct is attributed to presence of the bulky SiR_3 group. Different methodologies allow for synthesis of both symmetrical and unsymmetrical complexes. Thus, the mono-alkynyl complex $Ru_2(ap)_4(C{\equiv}CY)$ ($Y = SiMe_3$ or Si^iPr_3) could be reacted with $LiC{\equiv}CC{\equiv}CSiMe_3$ to give the mixed alkynyl complexes [32]. The presence of different silyl groups was notable since differential deprotection could be achieved via use of bases of differing strengths. The mono-deprotected complexes are of significant interest for subsequent Hay or Eglington coupling. A related series of bis-alkynyl complexes incorporating a ‘capping’ phenylacetylide ligand have also been synthesized [33].

The bis-alkynyl $Ru_2(ap)_4$ complexes are diamagnetic and exhibit well resolved ^{1}H- and ^{13}C-NMR spectra. The complexes are deep blue in color with peaks in the electronic absorption spectra at approximately 1030, 650, and 480 nm, which have been assigned as $\pi(Ru{-}N) \rightarrow \pi^*/\delta^*(Ru_2)$ and $\pi(C{\equiv}CR) \rightarrow \pi^*/\delta^*(Ru_2)$ transitions. Several single-crystal X-ray studies have been reported (Fig. 2) with a distinct lengthening of the Ru−Ru bond upon addition of the second alkynyl ligand. The cyclic voltammograms reveal three one-electron couples, one oxidation and two reductions. In THF these processes are centered approximately around 0.80, −0.50 and −1.50 V with complexes containing terminal $\equiv C{-}H$ groups showing poor reversibility. It is interesting to note that while the mono-alkynyl $Ru_2(ap)_4$ complexes show only a very weak peak for the $C{\equiv}C$ stretch, the bis-alkynyl complexes exhibit at least one very intense $C{\equiv}C$ stretch band around 2100 cm^{-1}. In comparison, organic alkynes [34] and most metallaynes [3] only exhibit weak $C{\equiv}C$ stretch bands. The appearance of significantly intensified $C{\equiv}C$ stretch band is likely attributed to a strong coupling between two *trans*-alkynyl ligands due to the extensive π-conjugation across the Ru−Ru bond.



(a)

(b)

Fig. 2. Structural plots of (a) $Ru_2(ap)_4(C_4SiMe_3)$ and (b) $Ru_2(ap)_4(C_4SiMe_3)_2$.

Bis-dinuclear complexes $[Ru_2(ap)_4]_2(\mu\text{-}C_{2n})$ ($n = 1$ or 2) were synthesized by addition of the bis-lithiated alkyne, either $LiC{\equiv}CLi$ or $LiC{\equiv}CC{\equiv}CLi$, to an excess of $Ru_2(ap)_4Cl$, and a single-crystal X-ray diffraction study of $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$ confirmed the μ-C,C′ bridging nature of the butadiyn-diyl ligand [35]. Linear polycarbon chains mediate significant electronic communication between the diruthenium centers, as indicated by cyclic voltammetry studies. For the $[Ru_2(ap)_4]_2(\mu\text{-}C_2)$ complex, the $K_{com}(-1)$ and $K_{com}(+1)$ values computed from voltammetric data (K_{com} is the comproportionation constant of mixed valent ion, see Ref. [36]) were 1.9×10^{11} and 6.6×10^4, respectively. For the $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$ complex, lengthening of the carbon chain bridge led to a decrease in both K_{com} values. $[Ru_2(ap)_4]_2(\mu\text{-}C_{2n})$ with $n = 4$ and 6 were recently obtained through the Hay coupling reaction of $[Ru_2(ap)_4](C_nH)$, and electrochemical studies indicated that the strength of electronic coupling further decreases with the increasing carbon chain length [37]. Large K_{com} values in the complexes of short carbon chain bridge imply high stability of the corresponding mixed valent species, both anionic and cationic, and intervalence charge transfer bands therein are being studied using spectroelectrochemical techniques.

A family of compounds analogous to the $Ru_2(ap)_4$ complexes is based on the $Ru_2(pfap)_4$ core [38], where pfap = 2,3,4,5,6-pentafluoro-2-anilinopyridinate.

Whereas the $Ru_2(ap)_4$ complexes exist only as the (4,0) isomer, $Ru_2(pfap)_4Cl$ was synthesized as a mixture of the (4,0), (3,1) and *trans*-(2,2) isomers, which were separated using column chromatography [38]. As with the (4,0) $Ru_2(ap)_4$ system, treating (4,0) $Ru_2(pfap)_4Cl$ with 50-fold $LiC{\equiv}CPh$ led to the isolation of both the mono- (40%) and bis-acetylide (40%) complexes. Reacting the (3,1) isomer of $Ru_2(pfap)_4Cl$ with 50-fold $LiC{\equiv}CPh$ resulted in the bis-acetylide as the dominant product (60%) along with the mono-acetylide as the minor product (7%). For the *trans*-(2,2) isomer, the same reaction conditions resulted in the bis-acetylide as the sole product in 85% yield.

X-ray diffraction studies of all three of the $Ru_2(pfap)_4$ bis-acetylide complexes conclusively proved the differing orientations of pfap ligands. A comparison of Ru–Ru bond lengths between (4,0) $Ru_2(ap)_4(C\equiv CPh)_2$ (2.471 Å) and (4,0) $Ru_2(pfap)_4(C\equiv CPh)_2$ (2.460 Å) indicates similar metal–metal bonding strength, although the Ru–C≡C– bonds are more distorted from linearity in the $Ru_2(ap)_4$ system [33]. Electrochemically the $Ru_2(pfap)_4(C\equiv CPh)_2$ complexes possess a single one-electron oxidation and two one-electron reductions. Progression from the (4,0) → (3,1) → (2,2) isomers results in a subtle change in $E_{1/2}$ values: anodic shift for the oxidation couple, and cathodic shift for both reductions. A comparison between (4,0) $Ru_2(ap)_4(C\equiv CPh)$ ($E_{1/2}(+1/0) = 0.24$ V, $E_{1/2}(0/-1) = -0.99$ V) and (4,0) $Ru_2(pfap)_4(C\equiv CPh)$ ($E_{1/2}(+1/0) = 0.80$ V, $E_{1/2}(0/-1) = -0.53$ V) shows a large anodic shift in the $E_{1/2}$ values of the $Ru_2(pfap)_4(C\equiv CPh)$ redox processes, which is clearly attributed to the electron-withdrawing nature of the fluorine substituents on the pfap ligand. As with the $Ru_2(ap)_4$ system, the parent chloro and the mono-acetylide $Ru_2(pfap)_4$ complexes are paramagnetic with $S = 3/2$, whereas the bis-acetylide complexes are diamagnetic.

Another extensively investigated series of diruthenium alkynyl complexes is based on the $Ru_2(DArF)_4$ core (DArF = diarylformamidinate). The initial complex $Ru_2(DPhF)_4(C\equiv CPh)_2$ (DPhF = diphenylformamidinato) was isolated from the reaction between $Ru_2(DPhF)_4Cl$ and excess $LiC\equiv CPh$ [39]. Subsequent investigation revealed that the mono-acetylide $Ru_2(DPhF)_4(C\equiv CPh)$ complex was also present in the reaction mixture, and the yields of both mono- and bis-acetylide compounds were optimized by varying the work-up conditions [40]. Modification of the aryl rings of DArF ligands with either donor or acceptor substituents enables tuning of electronic properties of the $Ru_2(DArF)_4$ acetylide complexes [41,42]. Treatment of $Ru_2(DmAniF)_4Cl$ (DmAniF = di(*m*-methoxyphenyl)-formamidinate) with three equivalents of $LiC\equiv CC\equiv CSiMe_3$ leads to the formation of the mono- and bis-butadiynyl complexes that can be separated on silica column [31].

X-ray diffraction studies of $Ru_2(DArF)_4(C\equiv CY)_n$ complexes confirm the generally cylindrical nature of both the mono- and bis-acetylide complexes (see Fig. 3), with the Ru–Ru bond lengthening upon alkynylation as encountered in the afore-mentioned diruthenium alkynyl systems. Similar to the $Ru_2(ap)_4$ system, $Ru_2(DArF)_4(C\equiv CY)$ is paramagnetic with $S = 3/2$, and its cyclic voltammogram consists of a single oxidation and a single reduction process. $Ru_2(DArF)_4(C\equiv CY)_2$ is diamagnetic, and exhibits a single oxidation and two reduction processes in its CV. Aryl substitution at the bridging DArF ligands may result in a pronounced shift of the redox potentials up to 713 mV. Although the $Ru_2(DArF)_4(CCPh)_n$ complexes are air and moisture stable, they decompose above 50 °C even under vacuum. In contrast, the linear poly-ynyl complexes $Ru_2(DArF)_4(C_4SiMe_3)_n$ exhibit much higher thermal stability [31].

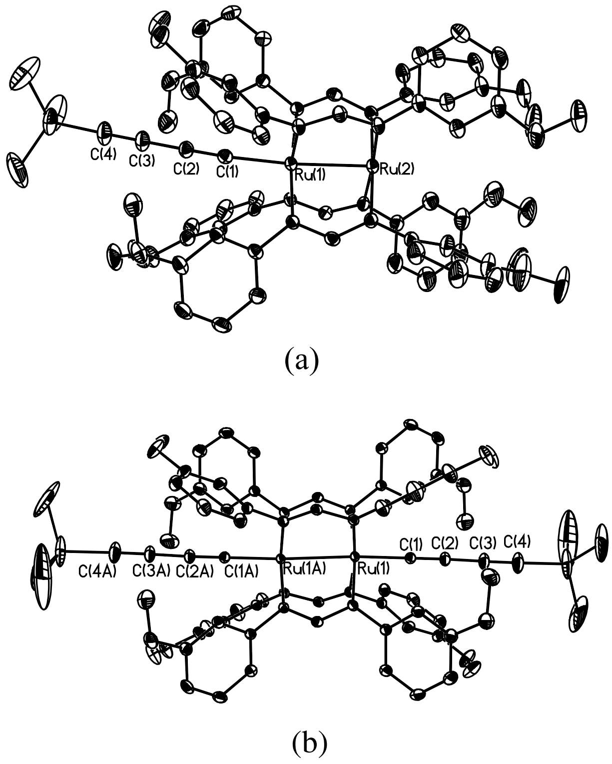


Fig. 3. Structural plots of $Ru_2(DmAniF)_4(C_4SiMe_3)$ and $Ru_2(DmAniF)_4(C_4SiMe_3)_2$.

Diruthenium alkynyl complexes have been investigated as 'molecular wires' because of both the electron-rich nature of the Ru_2 centers and the π-conjugation mediated by the poly-ynyl backbone. Selective desilylation of $Ru_2(DArF)_4(C_4SiMe_3)_2$ yielded $Ru_2(DArF)_4(C_4SiMe_3)(C_4H)$, which was homo-coupled to yield *trans*-$[(Me_3SiC_4)Ru_2(DPhF)_4]_2(\mu\text{-}C_8)$ [43]. The rigid rod nature of *trans*-$[(Me_3SiC_4)Ru_2(DPhF)_4]_2(\mu\text{-}C_8)$ was verified through a single crystal X-ray diffraction study (see Fig. 4). While the CV of the *trans*-$[(Me_3SiC_4)Ru_2(DPhF)_4]_2(\mu\text{-}C_8)$ exhibits richer features in comparison with that of $Ru_2(DArF)_4(C_4SiMe_3)_2$, it does not substantiate the 'molecular wire' claim due to the irreversibility of the observed couples. More recently, Kuhn et al. reported the synthesis of $Ru_2(DTolF)_4(4\text{-}C\equiv CC_5H_4N)_2$ (DTolF = *p*-tolylformamidinate), which serves as the bridging ligand between two $[Re(CO)_3(t\text{-}Bu_2bipy)]^+$ fragments to yield the tetra-metallic complex [44].

Another recent development in diruthenium acetylide chemistry has been the synthesis of $Ru_2(DMBA)_4(C\equiv$

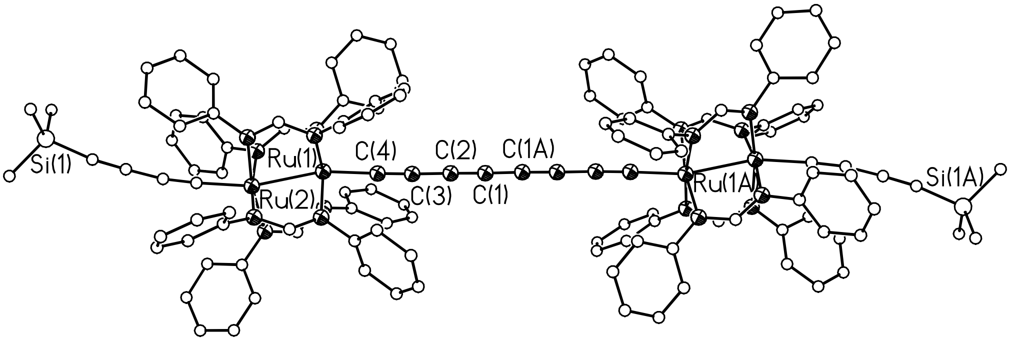
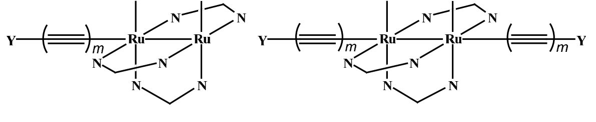


Fig. 4. ORTEP plot of *trans*-$\{(Me_3SiC_4)[Ru_2(DPhF)_4]\}_2(\mu\text{-}C_8)$ at 30% probability level generated from the data deposited with CSD.

$CY)_2$ type complexes (DMBA = *N*,*N′*-dimethylbenzamidinate) via treatment of the parent $Ru_2(DMBA)_4Cl_2$ complex with excess lithiated alkynyl ligands [45]. A clear advantage of $Ru_2(DMBA)_4$ complexes over the aforementioned Ru_2 complexes is a minimized steric crowding around the axial sites, which permits the synthesis of bis-adducts of C_2SiMe_3 [45] and C_2Fc on a $Ru_2(DMBA)_4$ core [46]. Unlike other diruthenium complexes, the mono-alkynyl complexes of a $Ru_2(DMBA)_4$ core could not be isolated. Cyclic voltammetric studies revealed that $Ru_2(DMBA)_4$ complexes are significantly more electron rich than other analogous Ru_2 compounds. Also unique to the DMBA-based compounds is the possibility of alkynylation under very mild conditions: $Ru_2(DMBA)_4X_2$ ($X = NO_3^-$ or BF_4^-) [47] react with terminal alkyne HC_2Y in the presence of Et_3N to yield $Ru_2(DMBA)_4(C_2Y)_2$. This synthetic route permits the isolation of both $Ru_2(DMBA)_4(C_2C_6H_4\text{–}4\text{-}SC(O)Ph)_2$ [46] and $Ru_2(DMBA)_4(C_2C_6H_4\text{–}4\text{-}NO_2)_2$ [48], which could not be prepared from the lithium salt route.

The diruthenium mono- and bis-alkynyl adducts represent two major structural motifs of interest (Scheme 3). While similarities in both structure and other physical properties can be found for compounds within each motif, significant contrast is noted between compounds belonging to different motifs. The fundamental difference between the mono- and bis-alkynyl motifs is in the electronic structure: the $S = 3/2$ ground state ($\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$) for the mono-species is converted to an $S = 0$ ground state ($\pi^4\delta^2\pi^{*4}$) upon addition of a second alkynyl ligand [49]. This change in the spin state is accompanied by concomitant changes in other physical characteristics. Peaks in the electronic absorption spectra undergo a dramatic red-shift upon proceeding from the Ru_2(II,III) system to the Ru_2(III,III) system due to a decrease in the energies of the ($\pi^*\delta^*$) manifolds following an increase in Ru_2 oxidation state. The redox behavior also changes due to the addition of the second alkynyl ligand, where the Ru_2^{7+}/Ru_2^{6+} couple is observed for the bis-species, but not the mono-species.



Scheme 3. Mono- (left) and bis-alkynyl compounds on a Ru_2 paddlewheel core.

3. Group 6 complexes

$M_2(PR_3)_4X_4$ type compounds are very common with M as Mo and W, and X as halides [14]. Hopkins et al. demonstrated that treating $M_2(PMe_3)_4Cl_4$ with four equivalents of $LiC{\equiv}CY$ resulted in the formation of $M_2(PMe_3)_4(C{\equiv}CY)_4$, where Y can be Me, ^{i}Pr, ^{t}Bu, $SiMe_3$ and Ph for M = Mo, and Me and ^{t}Bu for M = W according to the equation below [50,51]:

$$M_2(PMe_3)_4X_4 + 4LiCCY \rightarrow M_2(PMe_3)_4(CCY)_4 + 4LiX$$

It was shown later that $Mo_2(PMe_3)_4(C{\equiv}CSiMe_3)_4$ undergoes complete de-silylation in the presence of $(n\text{-}Bu_4N)(HF_2)$ to yield $Mo_2(PMe_3)_4(C{\equiv}CH)_4$ in 93% yield [52]. When only two equivalents of lithiated propyne was added to $W_2(PMe_3)_4Cl_4$, 1,1-$W_2(C{\equiv}CMe)_2Cl_2(PMe_3)_4$ was isolated in 15% yield [53]. Interestingly, combination of $Mo_2Cl_4(dmpm)_2$ (dmpm = bis(dimethylphosphino)methane) and a mixture of $LiC{\equiv}CSiMe_3$ and $HC{\equiv}CSiMe_3$ resulted in a compound that contains ligands η^1-C_2SiMe_3, $\mu,\eta^2{:}\eta^2$-HC_2SiMe_3, and μ-$C{=}C(SiMe_3)$-η^2-$CCSiMe_3$ derived from the coupling of two $(C{\equiv}CSiMe_3)^-$ anions [54]. Resonance Raman spectra of $M_2(C{\equiv}CY)_4(PMe_3)_4$ and crystal structures of $Mo_2(C{\equiv}CY)_4(PMe_3)_4$ with R as Me, $SiMe_3$ and ^{t}Bu and $W_2(C{\equiv}CMe)_4(PMe_3)_4$ were reported [55]. It has been suggested that examination of the $M\text{–}C{\equiv}CY$ bond distances in these complexes may be useful in determining the extent of $M\text{–}C{\equiv}CY$ π-interaction. Unfortunately, precise structural parameters required for this kind of analysis are not available due to frequent crystallographic disorders of Mo atoms encountered in these compounds [55]. Single-crystal structural studies confirmed the D_{2d} symmetry of the $M_2(PR_3)_4(C{\equiv}CY)_4$ complexes, with similar metal–metal bond lengths

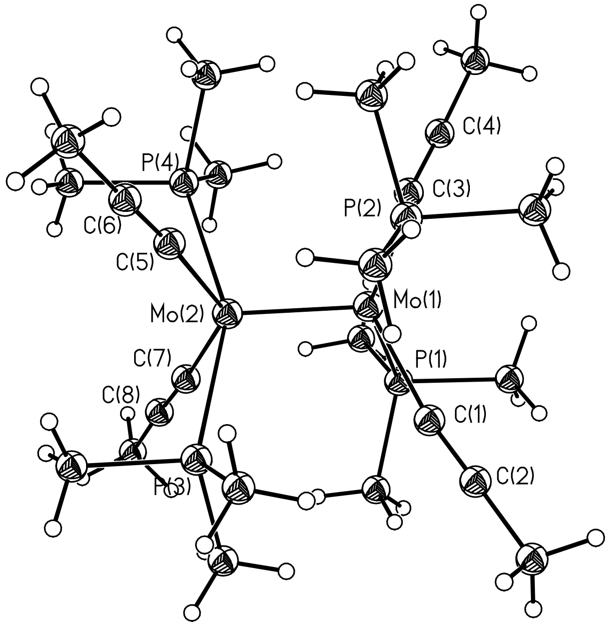
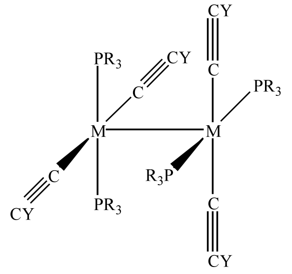


Fig. 5. ORTEP plot of $Mo_2(C{\equiv}CMe)_4(PMe_3)_4$ at 30% probability level generated from the data deposited with CSD.

among different alkynyl complexes of the same metal (see Fig. 5). The ditungsten analogues show a slight but progressive lengthening of the W–W bond from $W_2Cl_4(PMe_3)_4$ (2.262(1) Å) to $W_2(C{\equiv}CMe)_2Cl_2(PMe_3)_4$ (2.268(1) Å) to $W_2(C{\equiv}CMe)_4(PMe_3)_4$ (2.2760(8) Å). In several cases, strong threefold disorder prohibited accurate elucidation of many important bond lengths and angles [51], a phenomenon previously noted for other dimolybdenum complexes [56,57]. In addition, decomposition of the single-crystals in the X-ray beam was a recurring complication. The Mo–Mo bond length in $Mo_2(C{\equiv}CMe)_4(PMe_3)_4$ is significantly shorter (0.132 Å) than that of the ditungsten analog, an effect identical to that observed in the $M_2Cl_4(PMe_3)_4$ complexes (M = Mo or W) [58]. Comparison of selected bond lengths between dimolybdenum species is presented in Table 1. The lengthening of the Mo–Mo bond when proceeding from the chloro analog to the carbon-rich systems has been attributed to increased electron density on the dimolybdenum core [59].

These dimolybdenum and ditungsten complexes are blue or purple, and their thermal and air stability are dependant on the acetylide substituent (Ph < alkyl < $SiMe_3$). Impurities induced decomposition even when stored under an inert atmosphere. Tungsten complexes were less stable than analogous molybdenum complexes, with certain complexes also being light sensitive [51]. The complexes are diamagnetic and have been examined by ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy. Electrochemical investigation of $Mo_2(C{\equiv}CSiMe_3)_4(PMe_3)_4$ revealed a single reversible one-electron reduction at −2.13 V (vs. Fc) [60]. The $\nu(C{\equiv}C)$ has been demonstrated to be a sensitive probe of orbital mixing [55].

The family of dimolybdenum and ditungsten complexes synthesized by Hopkins et al. form their own unique structural motif (Scheme 4). Unlike other dimetallic systems with multiple acetylide ligands, none of the acetylide ligands in $M_2(C{\equiv}CY)_4(PR_3)_4$ are aligned in parallel with one another due to a variety of electronic and steric effects, and the complexes are broadly analogous to the organic tetraethynylethene. The structural motif differs from those reported for other complexes in that there are no bridging ligands, only the quadruple bond between the metal atoms. Despite stability problems, there is much potential for these systems: reactions with longer alkyne ligands such as butadiyne would be of interest, and mixed alkynyl complexes could be synthesized from the $M_2(C{\equiv}CY)_2Cl_2(PMe_3)_4$ precursor.



Scheme 4. Hopkins' Mo_2- and W_2-metallayes.

Table 1
Comparison of bond lengths (Å) among dimolybdenum species

	$Mo_2Cl_4(PMe_3)_4$ [a]	$Mo_2(Me)_4(PMe_3)_4$ [b]	$Mo_2(C{\equiv}CH)_4(PMe_3)_4$ [c]	$Mo_2(C{\equiv}CMe)_4(PMe_3)_4$ [d]
Mo–Mo	2.130(0)	2.1489(4)	2.134(1)	2.1406(8)
Mo–C	–	2.248(4)	2.157(4)	2.144(4)
C≡C	–	–	1.179(6)	1.197(5)

[a] Ref. [58].

[b] Ref. [59].

[c] Ref. [52].

[d] Ref. [55].

4. Dirhodium complexes

The first series of dirhodium acetylide complexes were synthesized by reaction between $Rh_2(ap)_4Cl$ and a series of sodium and lithium acetylides to give $Rh_2(ap)_4(C\equiv CY)$ where Y = H, Ph, C_5H_{11} and $C_4H_8C\equiv CH$ [61]. In contrast to the analogous $Ru_2(ap)_4$ series [30,33], a 5 fold excess of lithiated alkyne did not lead to alkynylation at the second axial site. Further work by Bear et al. led to the synthesis of $Rh_2(ap)_4(C_4SiMe_3)$ in 92% yield by the treatment of $Rh_2(ap)_4Cl$ with two equivalents LiC_4SiMe_3 [62]. $Rh_2(ap)_4(C_4Li)$, generated by treating $Rh_2(ap)_4(C_4SiMe_3)$ with 1.5 equivalents LiBu, was reacted with excess $Rh_2(ap)_4Cl$ to yield $[Rh_2(ap)_4]_2(\mu\text{-}C,C'\text{–}C\equiv CC\equiv C)$. These dirhodium complexes are air and light stable, and can be purified by silica gel chromatography.

The single-crystal X-ray diffraction study of $[Rh_2(ap)_4](C_2H)$ confirmed a lengthening of the Rh–Rh bond upon formation of the Rh–C bond [61]. Although the poor crystal quality prevented the refinement of structure, the skeleton of $[Rh_2(ap)_4]_2(\mu\text{-}C,C'\text{–}C\equiv CC\equiv C)$ can be discerned from the electron density map, and is very similar to that of $[Ru_2(ap)_4]_2(\mu\text{-}C,C'\text{–}C\equiv CC\equiv C)$ [35]. Unlike the Ru_2 system, $[Rh_2(ap)_4]_2(\mu\text{-}C_4)$ displays an electronic absorption spectrum closely resembling that of its 'half' molecule, $[Rh_2(ap)_4](C_2H)$ [61], reflecting the absence of a strong electronic coupling across the C_4-bridge.

The CV of the $[Rh_2(ap)_4](C_2Y)$ complexes consists of a single one-electron oxidation and one one-electron reduction attributed to the Rh_2(II,III)/Rh_2(III,III) and Rh_2(II,II)/Rh_2(II,III) couples, respectively [61]. Some trends may be noted when comparing redox-potentials between $Rh_2(ap)_4$ and $Ru_2(ap)_4$ complexes, as listed in Table 2.

Although both families exhibit similar redox processes, the $E_{1/2}$ values of the $Ru_2(ap)_4$ complexes are cathodically shifted when compared with the corresponding $Rh_2(ap)_4$ complexes. Furthermore, $[Rh_2(ap)_4]_2(\mu\text{-}C_4)$ exhibits a two-electron oxidation couple (2+/0) and a pair of one electron reduction couples ((0/−1) and (−1/−2)) that are separated by 130 mV. In comparison, $[Ru_2(ap)_4]_2(\mu\text{-}C_4)$ displays a pair of one electron oxidations of $\Delta E_{1/2} = 160$ mV, and a pair of one electron reductions of $\Delta E_{1/2} = 390$ mV [35]. The reduced electronic coupling between the Rh_2 centers across the C_4-bridge is probably due to an orbital-mismatch between the Rh and C centers.

5. Other dimetallic complexes

Dirhenium acetylide complexes $Re_2(\mu\text{-}H)(CO)_8(C\equiv CY)$ (Y = Ph and 4-$MeOC_6H_4$) were obtained via the metathesis reaction between $HC\equiv CY$ and $Re_2(\mu\text{-}H)(CO)_8(E\text{-}CH=CHEt)$ [63,64]. Subsequently, a series of complexes of the formula $Re_2(\mu\text{-}H)(CO)_7(dxpm)(C\equiv CY)$ (x = Ph or Me, Y = Ph or H) were prepared in good yield via photolysis of a mixture of the appropriate acetylene and $Re_2(\mu\text{-}dxpm)(CO)_8$ [65]. Interestingly, the dppm ligand may either be a chelate to a single Re atom or it may bridge between the two metal centers. Preparation of further dirhenium acetylide complexes demonstrated the enormous range of complexes that can be obtained by changing the Y group on the acetylide, or substitution on the Re core via displacement of CO [66–68]. The acetylide unit in the above complexes was in a fluxional bridging configuration as confirmed by both NMR spectroscopic and single-crystal X-ray structural studies. The ΔG value for the acetylide interchange process was determined by variable temperature NMR studies to be 10.5 kcal mol^{-1} for $Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}dppm)(C\equiv CH)$ [65] and 15.7 kcal mol^{-1} for $Re_2(CO)_7(\mu\text{-}H)(MeCN)(C\equiv CPh)$ [67], similar to that of related fluxional alkenyl complexes [69]. The Re–Re distances determined from X-ray diffraction studies range from 2.895 to 3.416 Å [65,67,68], which agree with a Re–Re single bond assignment. An ORTEP plot of $Re_2(CO)_7(\mu\text{-}H)(MeCN)(C\equiv CPh)$ is shown in Fig. 6. The Re–C(acetylide) distances range from 2.09 to 2.13 Å with the longest distance recorded for the σ-only acetylide, which is much longer than the averaged Re–CO distance (ca. 1.95 Å). The long Re–C(acetylide) bond is likely attributed to the lack of Re–C π-backdonation.

Analogous dimanganese acetylide complexes of general formula $Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-}dppm)(C\equiv CY)$ (Y = H, Ph, *t*-Bu and CH_3OCH_2) are also known [70]. Single-crystal X-ray studies confirmed the fluxional acetylide unit, but the exchange process was too fast to be determined, even at −90 °C. The complexes were

Table 2
Comparison of electrochemical potentials (V) between Ru_2 and Rh_2 complexes

	$[M_2(ap)_4C\equiv CH]$ [a]	$[M_2(ap)_4C\equiv CPh]$ [a]	$[M_2(ap)_4C_4SiMe_3]$ [b]	$[M_2(ap)_4]_2(\mu\text{-}C_4)$ [b]
Ru	1.30 [c], 0.20, −1.03	1.05 [c], 0.235, −0.985	0.48, −0.74	1.12 [c], (0.49/0.33), (−0.78/−1.17) V
Rh	1.03 [c], 0.38, −0.63	1.09 [c], 0.38, −0.62	0.66, −0.44	0.60, (−0.52/−0.65) V

[a] Solvent = CH_2Cl_2.
[b] Solvent = THF.
[c] Irreversible process.

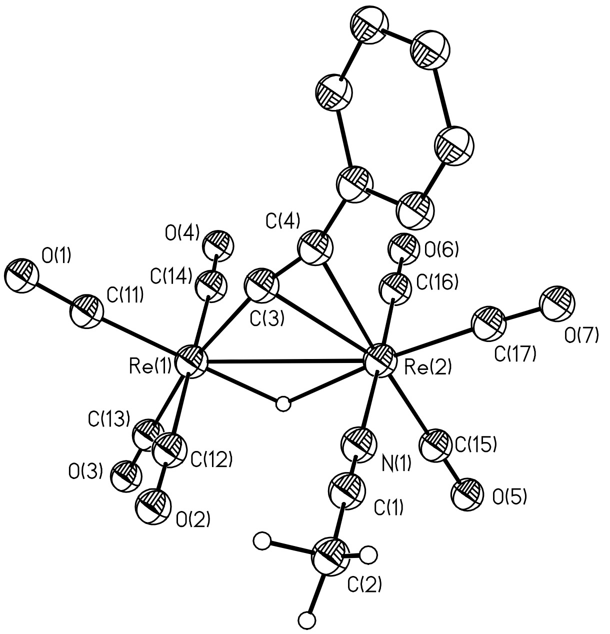


Fig. 6. ORTEP plot of $Re_2(CO)_7(\mu\text{-}H)(MeCN)(C{\equiv}CPh)$ at 30% probability level generated from the data deposited with CSD.

obtained by spontaneous isomerization of the bridging vinylidene ligand in the parent $Mn_2(CO)_6(\mu\text{-}dppm)(C{=}CHY)$ complex, with the reverse conversion from acetylide to vinylidene also being possible. Structural study of $Mn_2(CO)_6(\mu\text{-}H)(\mu\text{-}dppm)(C{\equiv}CPh)$ also revealed a long Mn–C(acetylide) bond (1.949 Å) in comparison with that of Mn–CO (ca. 1.8 Å).

A series of complexes of formula $M_2(\mu\text{-}PPh_2)(CO)_6(C{\equiv}CY)$ with M = Fe, Ru and Os have been synthesized by Carty et al., which provide insight into systematic variation of metals of the Group 8 series [71,72]. The reactivity of these complexes with amines [73] and nitriles [74] has also been investigated. X-ray diffraction studies of $M_2(\mu\text{-}PPh_2)(CO)_6(C{\equiv}CBu\text{-}t)$ (M = Fe, Ru, Os) permitted structural comparison among the Group 8 congeners. Although the metal–metal and metal–acetylide bonding distances were not unusual for each of the individual complexes, the η^2 acetylide–metal bond was observed to strengthen in the order of Fe < Ru < Os. The ΔG value for the acetylide interchange process was found to be in the range of 10.3–11.3 kcal mol^{-1}.

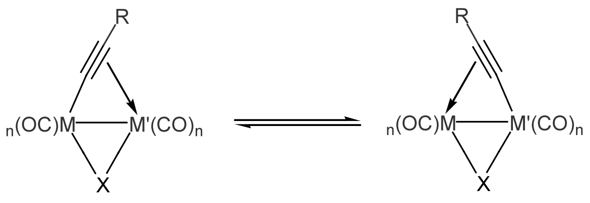
Green et al. reported dimolybdenum alkynyl complexes of the formula $[Mo_2(\mu\text{-}C{\equiv}CPh)(CO)_4(\mu^5\text{-}R)_2][N(PPh_3)_2]$ ($R = C_5H_5$ and C_9H_7) [75], where two Mo centers are singly bonded with a bridging phenyl acetylide unit. This type of complexes is related to the above bridging acetylide complexes, rather than the quadruply bonded $Mo_2(C{\equiv}CY)_4(PR_3)_4$ complexes of Hopkins et al. [50,52].

Puddephatt et al. reported a series of diruthenium complexes supported by bidentate phosphines, which are structurally dissimilar to that of the diruthenium 'paddlewheel' complexes. Addition of one equivalent $HC{\equiv}CY$ to $Ru_2(CO)_4(\mu\text{-}CO)(dppm)_2$ yielded an intermediate of proposed formula $[Ru_2(CO)_4(H)(C{\equiv}CY)(dppm)_2]$, which was converted to $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{\equiv}CY)Cl(dppm)_2]$ upon the exposure to a chlorinated solvent [76,77]. If $Ru_2(CO)_4(\mu\text{-}CO)(dppm)_2$ is reacted with more than one equivalent of $HC{\equiv}CY$, the second alkyne adds to become a σ-bonded alkenyl unit at one of two ruthenium centers. In the case of Y = Ph, a third acetylene ligand reacts to give a bridging vinylidene between the two ruthenium centers, which is unique in having three alkynyl ligands in three different coordination modes. X-ray diffraction studies revealed that the Ru–Ru distances are identical (2.914(3) Å) in the complexes with one and two bonded phenylacetylene ligands. The addition of a bridging vinylidene ligand between two ruthenium centers causes a contraction of the Ru–Ru bond length (2.853(1) Å).

The common structural motif among these $M_2(CO)_n(\mu\text{-}X)_m(C{\equiv}CY)$ complexes is what we have chosen to call 'fluxional diamond' structures (see Scheme 5), which are structurally related to the dialkynyl 'tweezer' complexes recently reviewed by Lang et al. [5]. The most notable feature of these complexes is the rapid fluxional interchange of the acetylide ligand between the metal centers. A secondary feature is the bridging ligand, which may link the metal centers through a single atom bridge (μ-H or PPh_2), a two-atom bridge ($\mu\text{-}C_5H_4N$) or a three-atom bridge (μ-dppm or μ-dmpm). Alternatively there may be a mix of several bridging ligands in the same complex. This combination of ligands and bonding modes makes this an interesting and unique structural motif.

6. Conclusions

The homo-dimetallic alkynyl complexes reviewed here are clearly dominated by both the Ru_2 and Rh_2 paddlewheel species, and the quadruply-bonded $M_2P_4(C{\equiv}CY)_4$ type compounds. Compounds from both categories are electron rich at the metal centers, and typically exhibit multiple redox couples, which should enable them to serve as useful electron reservoirs in redox active polymers and supramolecules. Because of the presence of one or more metal–ligand charge



Scheme 5. 'Fluxional diamond' motif.

transfer transitions, these compounds are often deeply colored, and hence can be utilized as chromophores as well. In addition, the mono-alkynyl Ru_2 compounds are $S = 3/2$ molecules, based on which bulk magnetic materials may be built if a significant ferromagnetic coupling can be realized. It is also noted that the paddlewheel motif is the most prevailing structural motif for homo-dinuclear compounds containing M–M bonds [14], and the success in alkynylation of dinuclear compounds at the axial positions may be extended beyond Ru_2 and Rh_2 species. For instance, the Re_2 paddlewheel species exhibit high tendency towards axial ligation, and axial alkynyl compounds should be expected. Using Ru_2-alkynyl compounds as a ligand, as reported recently by Kuhn et al. [44], represents a new development in inorganic supramolecular chemistry.

While these compounds exhibit promising attributes as candidates for electronic and opto-electronic materials, several issues related to practical applications, such as stability, solubility, and cost, need to be considered as well. While Ru_2 and Rh_2-based alkynyl complexes are quite stable towards air and moisture, the $M_2P_4(C{\equiv}CY)_4$ complexes (M = Mo and W) are more susceptible to degradation in ambient atmosphere. Clever molecular engineering is needed to further stabilize the latter class of compounds. Paddlewheel compounds can be readily derivatized via aromatic substitution at the bridging ligand [78], which facilitates solubility tuning. More importantly, further assembly of these dinuclear alkynyl complexes into linear oligomers and other supramolecules necessitates a high yield ≡C–H coupling chemistry. While the feasibility of the Glaser coupling reaction has been demonstrated [35,37], applicability to general dinuclear alkynyl complexes remains to be explored. Furthermore, there is only a limited understanding about the electronic structure of M_2–alkynyl complexes, and the ground state configuration of Ru_2-based compounds was described as ‘enigmatic’ [79]. Clearly, these issues have to be resolved on the basis of first principle calculations.

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